Effects of Gamma Radiation on Polymer in Solution. (V) : Intra-Molecular Crosslinking of Poly (Acrylic Acid) in Dilute Aqueous Solution (Special Issue on Physical, Chemical and Biological Effects of Gamma Radiation, IV)

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Effects of Gamma Radiation on Polymer in Solution. (V) Intra-Molecular Crosslinking of Poly(Acrylic Acid) in Dilute Aqueous Solution.

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The previous work has shown that gelation of poly(acrylic acid) in solution occurs most readily in acid form in the presence of 0.01N NaCl. The present investigation has been carried out to elucidate in more detail the mechanism of crosslinking occurring in these concentration ranges. Irradiation of the deaerated solutions below the critical concentration led to main-chain scission when NaCl concentrations of solutions to be irradiated were lower than 0.01N. However, in the case of the solutions containing NaCl above 0.01N, the solutions became turbid on irradiation. Detailed studies on properties of these turbid solutions have revealed that the origin of turbidity can be attributed to the formation of intra-molecular crosslinking. The reduced viscosities of the intra-molecular-crosslinked polymer were considerably lower than those of the linear polymer over the polymer concentration range studied; and the increase in the reduced viscosity usually observed at lower concentrations was very slight in the case of intra-molecular-crosslinked polymer. The values of pH of the intra-molecular-crosslinked polymer were higher than those of the linear polymer. The present study confirms the conclusion in the previous paper that the crosslinking of polyelectrolyte in aqueous solutions can be explained only in terms of both the change in expansion and the repulsion due to ionized groups.

INTRODUCTION

Effects of ionized group content and added salt on crosslinking of poly(acrylic acid) (PAA) in aqueous solutions, described in the previous paper[1], may be summarized in Fig. 1. These two variables are put together in Fig. 1 in such a fashion that the expansion of polyion increases in the rightward direction of abscissa. Assuming that, in the left-hand region from the minimum of the curve, the effect of varying size of polymer predominates over the effect of repulsion, while in the opposite region the effect of repulsion prevails, one was able to explain the change in the critical concentration. Obviously, properties of the net-work gel produced on irradiation of solutions above a critical concentration may be independent of whether formation of the gel is influenced by the effect of repulsion or the effect of varying size. On the other hand, below the critical concentration, reactions induced by irradiation of dilute solutions may be possibly influenced by these two competing effects. When solutions are irradiated below the critical concentration, as is well known, a continuous macro-gel is

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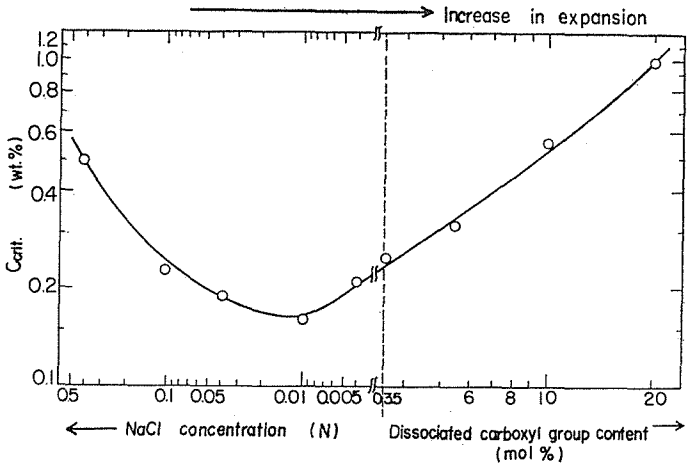

Fig. 1. Influence of the charge density of PAA of the critical concentration $C_{crit.}$ for gel-formation.

never formed, but either a micro-gel-formation[2,3] or degradation takes place. In the case of polyelectrolyte, it may be expected that, if the repulsion is strong enough, polymers exhibit no micro-gel-formation, but only degradation.

The present work was undertaken to find out what sorts of reactions are occurring under irradiation of dilute solutions below the critical concentration and to confirm the above supposition that crosslinking of polyelectrolyte is influenced by two competing effects, that is, repulsion and variation in size.

EXPERIMENTAL

PAA samples used, irradiation procedures and methods of viscosity measurements were quite the same as described in the previous paper[1]. When it was necessary to remove the added salt fom the irradiated solutions, they were passed through two columns filled with a cation-exchange resin, Amberlite IR-120, and an anion-exchange resin, Amberlite IR-45.

The relative turbidity of solutions observed during irradiation was estimated from an equation $\tau = 2.3 \log I_1/I_0$, where I_0 and I_1 are the intensities of the light scattered in a direction of 90° from the direction of an incident ray for the solution before and after irradiation, respectively. The intensity was measured at a polymer concentration of 0.1% using an electrophotometer.

Potentiometric titrations were performed at room temperature with a P-type pH meter (manufactured at Horiba Instruments Inc., Kyoto). The solution to be titrated was stirred on a magnetic stirrer, the stirrer being stopped for each reading. Each titration was made with a period of a few minutes between successive readings, as the pH became constant almost instantaneously after the addition of a base (0.01N NaOH).

RESULTS

It has been found in the studies on poly(vinyl methyl ether)[4] that irradiation

of the polymer in aqueous solutions below a critical concentration does not lead to formation of a continuous gel, but makes the solutions turbid. This suggests the plausible transformation of molecular configuration in solutions due to formation of intra-molecular crosslinkings during irradiation. It is of interest to see whether the intra-molecular crosslinking can be also formed in the PAA solutions where intra-molecular repulsive force exists

1) **Occurrence of Turbidity under Irradiation**

When the ionic strength of solutions exceeded a certain value, the solutions became turbid under irradiation. The solutions before irradiation were, of course, transparent independently of the presence and the absence of NaCl. The relative turbidity of solutions of PAA irradiated in acid form at a polymer concentration of 0.1 wt.% in the absence of air is shown in Fig. 2. The ionic strength was

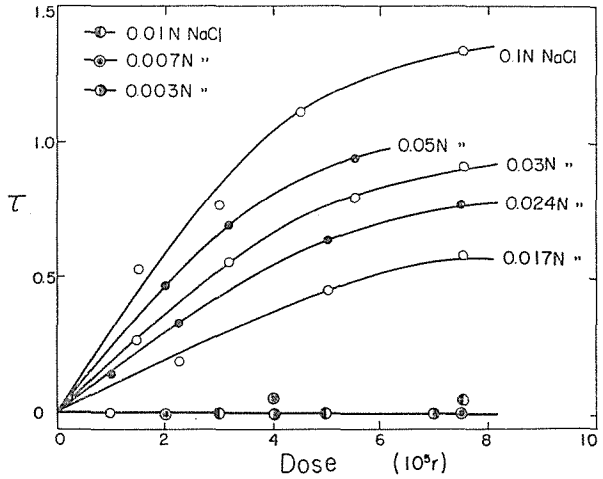

Fig. 2. Relative turbidity τ as a function of radiation dose for PAA irradiated in the absence of air and in 0.1% solution with various amounts of added NaCl.

adjusted by addition of appropriate amounts of NaCl. The turbidity was measured without removing from the irradiated solution the NaCl which was present during irradiation, because the presence of NaCl seemed not to affect the turbidity. If a sufficient amount of air was dissolved in the solutions to be irradiated, turbidity did not occur, however large a dose was used. From Fig. 2, the relative turbidity appears to approach an upper limit as the irradiation proceeds.

To demonstrate more clearly the relation between ionic strength and turbidity, initial slopes of the curves in Fig. 2 were plotted against NaCl concentration in Fig. 3. It is of particular interest to note that the minimum concentration of NaCl needed for the incipient occurrence of turbidity agrees exactly with the NaCl concentration corresponding to the minimum critical concentration which Fig. 1 shows. It is clear that solutions become turbid only when irradiated at NaCl concentrations above 0.01N. This finding affords a support to the expectation above mentioned that either of the two different reactions would occur preferentially in each range of NaCl concentration below and above 0.01N.

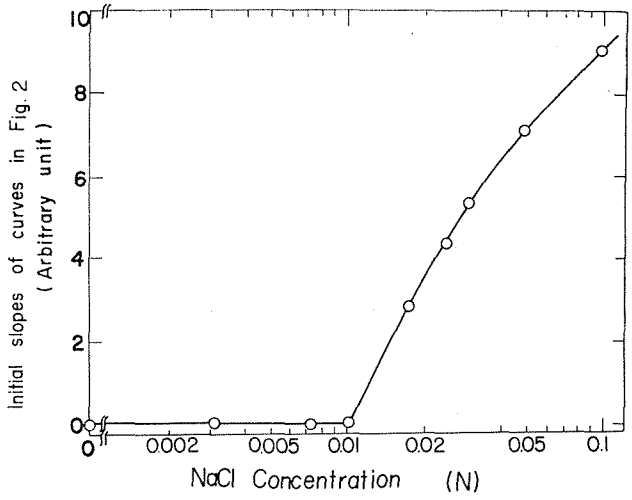

Fig. 3. Effects of NaCl concentration on the turbidity occurring during irradiation.

2) Viscometric Behavior of Irradiated Polymer

Occurrence of the turbidity may be attributed mainly either to aggregation of polymers or to more tightly coiled configuration of polymers. The latter may be brought about by the formation of intra-molecular crosslinking unless solvent power remains constant during irradiation. The transformation of the molecular configuration is expected to affect necessarily hydrodynamic properties such as solution viscosity. Fig. 4 shows limiting viscosity numbers measured in 0.1N NaCl of various PAA's obtained on irradiation under the following conditions; (a) in aerated salt-free solution, (b) in aerated 0.1N NaCl solution, (c) in deaerated salt-free solution, (d) in deaerated 0.1N NaCl solution. As can be seen from Fig. 4, the limiting viscosity number decreases with radiation dose in all cases regardless of the irradiation conditions. The presence of air and the absence of NaCl in solutions to be irradiated caused the limiting viscosity number to fall

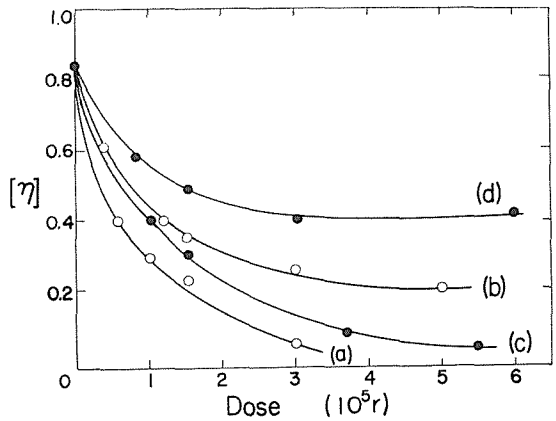

Fig. 4. Changes in limiting viscosity number [η] during irradiation of 0.1% solution under various conditions (a)~(d): for the conditions, see the text.

more rapidly. Among the four different cases (a) to (d), occurrence of turbidity was observed only when radiation was exposed to deaerated 0.1N NaCl solution, *i.e.*, the case (d). Furthermore, in this case, solution viscosities decreased most slowly. If the viscosity-drop can be assumed to be owing to main-chain scission, the reciprocal of degree of polymerization should increase linearly with increasing radiation dose, as theoretically expected. These plots are shown in Fig. 5, where it is seen that in the cases (a), (b) and (c) where the solution remained transparent during irradiation, a linearity was observed. On the other hand, in the

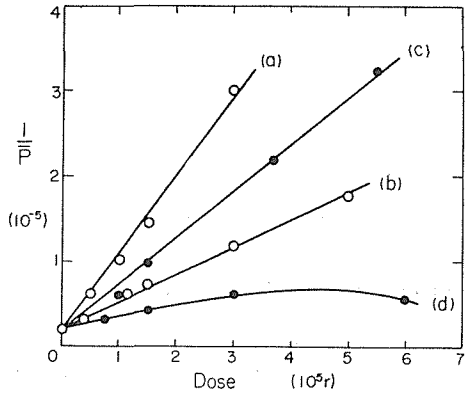

Fig. 5. Reciprocal of the degree of polymerization $\overline{P}$ as a function of radiation dose for PAA irradiated under various conditions.

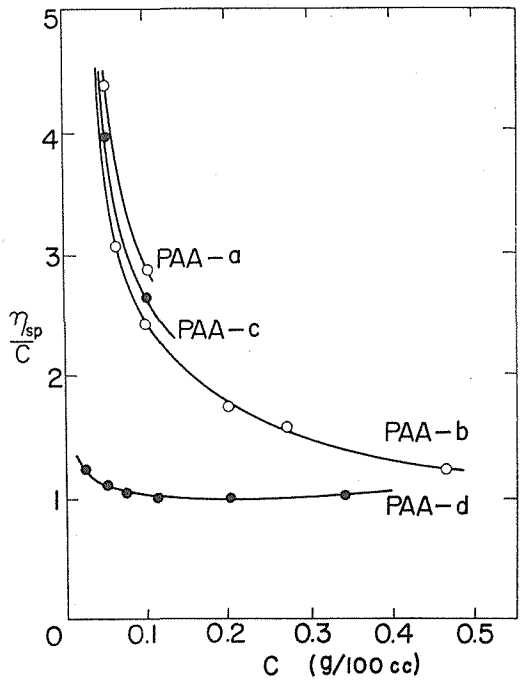

Fig. 6. Concentration dependence of reduced viscosity for the irradiated PAA: for the irradiation condition, see the text. Viscosities were measured in the absence of added salt.

case (d) where the irradiated solutions became turbid, the curve was found not to be linear, which implies occurrence of a reaction different from the main-chain scission. It is probably the intra-molecular crosslinking.

In order to ascertain the formation of intra-molecular-crosslinked polymer, viscometric behaviors were examined for the polymers obtained under the same condition as above described except the radiation dose. Irradiation time was controlled in such a way that all the limiting viscosity numbers of these polymers in 0.1N NaCl are exactly identical. For simplicity, these polymers were designated according to the irradiation condition as follows; PAA-a, irradiated at 5.0×10^4r, in aerated salt-free solution; PAA-b, at 1.1×10^5r in aerated 0.1N NaCl solution; PAA-c, at 1.0×10^5r in deaerated salt-free solution; PAA-d, at 3.0×10^5r in deaerated 0.1N NaCl solution. As noted above, only in the case of PAA-d, the solution became turbid under irradiation. Plots of the reduced viscosity against the polymer concentration are given in Fig. 6. It is evident that the reduced viscosities of PAA-a, -b and -c in the absence of added salt rise very sharply at lower polymer concentrations similarly to those of PAA before irradiation. However, for the PAA-d, the reduced viscosities increase only very slightly even at the considerably low concentrations.

3) Potentiometric Behavior of Irradiated Polymer

Solution properties of the irradiated PAA were, further, examined by means of a potentiometric titration. Fig. 7 shows titration curves for the various irradiated PAA polymers. The polymers studied here are the unirradiated PAA, PAA-b and PAA-d. The titration was carried out at a 0.01N concentration of polymer with NaOH in the absence of added salt. Plots of pH as a function of

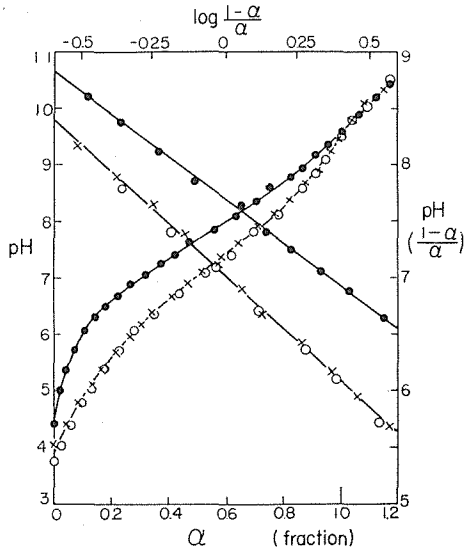

Fig. 7. Titration curves and Henderson-Hasselbalch plots for the unirradiated PAA (○), PAA-b (×) and PAA-d (●): for the irradiation and measurement conditions, see the text.

$\log \frac{1-\alpha}{\alpha}$, basing on a modified Henderson-Hasselbalch equation, $pH = pK_{av} - n \log \left(\frac{1-\alpha}{\alpha}\right)$, where α is the degree of neutralization, n is a constant and K_{av} is the average ionization constant, are also shown for these titrations. As can be seen from Fig. 7, the values of pH of PAA-d are clearly higher than those of the unirradiated PAA and PAA-b, both of which are virtually identical. In every case, Henderson-Hasselbalch plots of the data give straight lines in the range of $70\% > \alpha > 30\%$. The intercepts and the slopes of these straight lines indicate that pK_{av} and n of both the unirradiated PAA and PAA-b are 7.0 and 2.4, respectively; and pK_{av} and n of PAA-d are 7.7 and 1.9, respectively. Evidently, there is a noticeable difference in pK_{av} between PAA-d and PAA-b or the unirradiated PAA.

DISCUSSION

The significant difference in viscometric behaviors between the PAA-d and the PAA-a, -b and -c may be attributed undoubtedly to the difference in chain structure. The content of carboxyl groups seems to vary, if so, only to a negligible extent under irradiation in the radiation dose range investigated here. An examination of Fig. 6 reveals that curves of PAA-a, -b and -c are approximately identical and have the shape characteristic to the linear PAA. From this observation and Fig. 5, it may be concluded that the viscosity-drops of these polymers shown in Fig. 4 may be attributed to the main-chain scission. Furthermore, the fact shown in Fig. 6 that the reduced viscosities of PAA-d are always much lower than those of the PAA-a, -b and -c can be regarded undoubtedly as an evidence showing that in the case of PAA-d there is restrictive force upon extensions of the polymer coil. This restrictive force is supposed to be owing to the intra-molecular crosslinking formed under irradiation. As a conclusion, the occurrence of turbidity in solutions can be attributed to the formation of the intra-molecular-crosslinked polymer, namely, the micro-gel.

A further confirmatory evidence for the existence of the micro-gel can be given by the result shown in Fig. 7 that the average ionization constant of the PAA-d is noticeably higher than that of the PAA-b. This difference may be explained as follows. Since the concentration of ionizable carboxyl groups in a volume element is higher with the crosslinked than the linear polymers, suppression of ionization of COOH caused by COO^- becomes larger with the crosslinked polymers, and hence the hydrogen ion concentration decreases in the solution of the crosslinked polymer, leading to the larger ionization constant for the crosslinked polymer.

Although the formation of the intra-molecular crosslinking was clarified only in the case of the PAA-d which was obtained on irradiation of 0.1N NaCl solution, it seems quite reasonable to expect that the intra-molecular crosslinking can be always formed if the NaCl concentration of solutions is higher than 0.01N. The reason for this is that, in this concentration range, the solutions became turbid under irradiation similarly to the case of the PAA-d. Thus, it can be concluded that the reaction actually taking place under irradiation of the

the deaerated solution below the critical concentration depends on whether NaCl concentration is below or above 0.01N. Namely, when the NaCl concentration is below 0.01N, the reaction occurring is the main-chain scission and when it is above 0.01N, the intra-molecular crosslinking occurs.

The result shown in Fig. 1 could be explained in the previous work reasonably on the basis of the following assumption. In a low ionic strength range below 0.01N NaCl, the repulsion, which prevents the radical combination, may influence the crosslinking most significantly. On the other hand, when the NaCl concentration becomes higher than 0.01N, the diminution of polyion expansion with increasing ionic strength may become more important than the effect of repulsion. This assumption is strongly supported by the conclusion above cited. The result that the degradation occurs exclusively in the NaCl concentration range below 0.01N may be explained as being due to the repulsion which prevents the formation of crosslinking. Similarly, the result that the formation of intra-molecular crosslinking becomes possible in the range above 0.01N NaCl may be explained in terms of the remarkable decrease in repulsion. Increasing rate of the crosslinking with higher ionic strength may be due to the well-known fact that higher ionic strength leads to more tightly coiled configuration, so that the intra-molecular crosslinking can be formed more efficiently.

It may be unavoidably necessary for the micro-gel-formation that polymer coils are only partially in contact with each other in the solution or not at all.

Therefore, the maximum concentration, below which the micro-gel-formation becomes possible, may correspond to a concentration at which polymers begin to interfere with each other, if degradation does not occur and the repulsion force is not so intense as to prevent the radical recombination. Such conditions may be satisfied only in the case of the solution containing NaCl above 0.01N and no air. If this is ture, it will be possible to estimate the expansion of polyion from the value of critical concentration on the assumption of closed packing array, as described in the previous paper[5]. The radii of PAA in 0.1N NaCl shown in Fig. 1 are given in Table 1. The radius in the third column is

Table 1. Expansions of polyion calculated using crosslinking data and Einstein's formula.

NaCl conc. of solution for irradiation	Initial $[\eta]$ of the solution	Radius of PAA	
		from the critical conc.	from Einstein's formaula
0.1N	0.80	374Å	173Å
0.4N	0.50	288Å	148Å

calculated using the data of the critical concentration for gel-formation, and the radius in the last column is the hydrodynamic effective radius calculated from Einstein's formula. Obviously, there is nearly two times difference between the radii calculated from the two different methods. The similar result was also obtained in the study on PVAG[5]. This difference is not surprising if one considers the physical meanings of these two radii. In this respect, datailed

discussion will be presented in the subsequent paper.

Hitherto, the decrease in viscosity observed during irradiation of dilute aqueous solutions has often been attributed to the formation of the intra-molecular crosslinking, of course, except the case where the main-chain scission undoubtedly occurs. However, there has been no direct support for the existence of these intra-molecular crosslinkings. The decrease in viscosity is only a necessary, but not sufficient evidence for the crosslinking. In order to examine the formation of this crosslinking, it seems most promising to determine the molecular weight change during irradiation. In the aqueous systems, however, it is known to be rather difficult to determine the absolute value of molecular weight by means of light scattering or osmotic pressure measurement. Recently Dieu and Desreux[3,6] have studied the change in sedimentation constant and limiting viscosity number occurring during irradiation of poly(vinyl alcohol) (PVA) in dilute aqueous solutions. They found that, in higher dose range, the viscosity of irradiated PVA decreased with dose, whereas the sedimentation constant increased, demonstrating the formation of more symmetrical molecular clusters, or micro-gel particles. It seems to us that this is an only study which gave the strong evidence for the formation of the intra-molecular crosslinking. In our case, the existence of the intra-molecular crosslinking could be confirmed by determination of the viscosity or the potentiometric titration, by taking advantage of electrostatic property of ionized groups among a polymer chain.

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